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<p>(54) Title: <b>CLEANING COMPOSITION AND METHOD FOR REMOVING RESIDUES</b></p> <p>(57) Abstract</p> <p>Non-corrosive cleaning compositions that are aqueous based and useful for removing photoresist, plasma etch and CMP residues from a substrate. One preferred cleaning composition comprises: (i) a hydroxylamine or a hydroxylamine salt compound; (ii) at least one fluorine-containing compound; and (iii) water. Another cleaning composition comprises: (i) a compound selected from the group consisting of: an amine, a quaternary ammonium hydroxide, and ammonium hydroxide; (ii) at least one fluorine-containing compound; and (iii) water.</p>		

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## CLEANING COMPOSITION AND METHOD FOR REMOVING RESIDUES

### BACKGROUND OF THE INVENTION

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#### Field of The Invention

This invention relates to a cleaning composition and method for use in microelectronics manufacturing, and more particularly to a non-corrosive cleaning composition and method for removing photoresist, plasma etch and chemical-  
10 mechanical polishing (CMP) residues on substrates.

#### Description of Art

In the manufacture of microcircuits, positive photoresists are used as an intermediate mask for transferring an original mask pattern of a reticule onto wafer  
15 substrates by means of a series of photolithography and plasma etching steps. One of the steps in the microcircuit manufacturing process is the removal of the patterned photoresist films from the substrates. In general, this step is affected by one of two methods. One method involves a wet stripping step in which the photoresist-covered substrate is brought into contact with a photoresist stripper  
20 solution that consists primarily of an organic solvent and an amine. However, stripper solutions cannot completely and reliably remove the photoresist films, especially if the photoresist films have been exposed to UV radiation and plasma treatments during fabrication. Some photoresist films become highly cross-linked by such treatments and are more difficult to dissolve in the stripper solution. In  
25 addition, the chemicals used in these conventional wet stripping methods are sometimes ineffective for removing inorganic residual materials formed during the plasma etching of metal or oxide layers with halogen-containing gases.

An alternative method of removing a photoresist film involves exposing a  
30 photoresist-coated wafer to oxygen plasma in order to burn the resist film from the substrate surface in a process known as oxygen plasma ashing. Oxygen plasma ashing has become more popular in the microcircuit manufacturing process

because it is carried out in a vacuum chamber and, hence, is expected to be less susceptible to airborne particulate or metallic contamination. However, oxygen plasma ashing is also not fully effective in removing plasma etching residues noted above. Instead, removal of these plasma etching residues must be accomplished by subsequently exposing the photoresist film to certain alkaline solutions. Several commercial products are now available to clean the plasma etching residues left by plasma etching followed by oxygen ashing. For example, EKC 265, available from EKC Technology, Inc., is a plasma etching cleaning solution composed of water, alkanolamine, catechol and hydroxylamine. Such a composition is disclosed in U.S. Patent No. 5,279,771 to Lee. ACT 935, available from Ashland Chemical, is another plasma etching cleaning solution and is composed of water, alkanolamine and hydroxylamine. In both cases, hydroxylamine is used as a corrosion inhibitor. R-10, a post-strip rinse available from Mitsubishi Gas Chemical, is composed of water, alkanolamine and a sugar alcohol, wherein the sugar alcohol acts as a corrosion inhibitor.

Although these commercial products can effectively dissolve plasma etching residues, the combination of water and alkanolamine contained therein can also attack the metallic layers deposited patternwise on the substrate. The addition of a corrosion inhibitor to these products can mitigate to a certain extent, the unwanted attack on the metallic layers and oxide layers deposited on the substrate. However, since these products have a pH above 11, even in the presence of a corrosion inhibitor, they may attack certain corrosion-sensitive metal layers. Particularly, metal layers such as aluminum or aluminum alloys (e.g., Al-Cu-Si), titanium nitride, titanium tungsten and the like are particularly corrosion sensitive. Furthermore, while the addition of a suitable corrosion inhibitor is essential to prevent corrosion of the substrate metal layers, the corrosion inhibitor must not inhibit the removal of the plasma etching residue.

It is difficult to balance effective plasma etching residue removal and corrosion inhibition because chemical compositions of the plasma etching residues

are generally similar to those of the metal layers or oxide layers on the substrate. The alkanolamine used in the prior art cleaning compositions was oftentimes found to attack both the plasma etching residue and the substrate metal layers. Moreover, if a post-cleaner rinse such as isopropyl alcohol was not used, the corrosion could be very severe. In addition, some types of the corrosion inhibitors have been found to retard plasma etching residue removal. There has also always been a tradeoff between speed of plasma etching residue removal and substrate metal layer corrosion inhibition. Accordingly, there has remained a need for a method of quickly and effectively removing the plasma etching residues without causing metal layer corrosion.

Several other patents in the photoresist stripper/cleaner application field exist as follows, although none of them disclose the use of the method or compositions of the present invention:

Japanese Patent Application No. 7-028254, assigned to Kanto Kagaku, discloses a non-corrosive resist removal liquid comprising a sugar alcohol, an alcohol amine, water, and a quaternary ammonium hydroxide.

PCT Published Patent Application No. WO 88-05813 teaches a positive or negative photoresist stripper containing butyrolactone or caprolactone, quaternary ammonium hydroxide compound, and optionally, a nonionic surfactant.

U.S. Patent No. 4,239,661 to Muraoka et al. discloses a surface-treating agent comprising an aqueous solution of 0.01% to 20% trialkyl (hydroxyalkyl) ammonium hydroxide. This agent is useful in removing organic and inorganic contaminants deposited on the surface of intermediate semiconductor products.

U.S. Patent No. 4,904,571 to Miyashita et al. teaches printed circuit board photoresist stripper composition containing a solvent (e.g., water, alcohols, ethers, ketones, and the like), an alkaline compound dissolved in the solvent, including

quaternary ammonium hydroxide, and a borohydride compound dissolved in the solvent.

U.S. Patent No. 5,091,103 to Dean et al. teaches a positive photoresist stripping composition containing: (A) N-alkyl-2-pyrrolidone; (B) 1,2-propanediol; and (C) tetraalkylammonium hydroxide.

U.S. Patent No. 5,139,607 to Ward et al. teaches positive and negative photoresist stripping composition containing: (A) tetrahydrofurfuryl alcohol; (B) a polyhydric alcohol (e.g., ethylene glycol or propylene glycol); (C) the reaction product of furfuryl alcohol and an alkylene oxide; (D) a water-soluble Bronstead base type hydroxide compound (e.g., alkali metal hydroxide, ammonium hydroxide and tetramethyl ammonium hydroxide); and (E) water. Optionally, the composition may also contain up to 1% of a nonionic surfactant.

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U.S. Patent No. 5,174,816 to Aoyama et al. discloses a composition for removing chlorine remaining on the surface of an aluminum line pattern substrate after dry etching, which composition comprises an aqueous solution containing 0.01 to 15% by weight of a quaternary ammonium hydroxide, such as trimethyl (2-hydroxyethyl) ammonium hydroxide, and 0.1 to 20% by weight of sugar or sugar alcohol, such as xylitol, mannose, glucose and the like.

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In addition to photoresist and plasma etch removal, another step that is widely used in the manufacturing of microcircuits includes a planarization process such as planarization etch back or chemical-mechanical polishing (CMP). A planarization process is needed in microcircuit manufacturing because the deposition of successive layers of materials on the substrate causes the surface to become uneven and it is difficult to lithographically print images over the uneven topography. The planarization process evens the surface making it easier to form an image thereon by lithographic printing.

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In planarization etch back, a planarizing material, such as a polymer resist or a spin on glass (SOG) containing  $\text{SiO}_2$  is typically spun on the uneven topography to planarize the substrate. The substrate is then subjected to a plasma etch process wherein the planarizing material and underlying substrate are etched at approximately the same rate to form a planar surface. With this process, the plasma etch residues and portions of the planarizing material typically remain on the substrate and must be removed.

In the CMP process, the surface that is to be planarized is brought into contact with a rotating polishing pad in the presence of an abrasive slurry. A portion of the surface layer of the substrate is removed by the chemical nature of the slurry and the abrasive action of the polishing pad. The problem with CMP is that residues are left behind on the substrate, either from the slurry that is used in the CMP process or from detached substrate material. These residues can contaminate the vias, and deleteriously affect the workings of the microcircuit. Especially severe contaminants to microcircuits are residues from the polishing slurry which contain metal contaminants including alkaline metals such as sodium, potassium, and the like, and iron.

The CMP contaminants are typically removed from the substrate surface by contacting the surface with a caustic solution containing ammonium hydroxide or ammonium hydroxide mixed with hydrogen peroxide. In addition, brush scrubbing with these solutions has also been used to remove particulate matter. However, these caustic solutions can diffuse through defects in the substrate and attack the metal layers such as aluminum, aluminum alloys, refractory metals, and the like. The metal attack may subsequently cause voids in the metal that can lead to failure of the microcircuit.

Several patents describe attempts of solving the problem of metal attack using the combination of a specific organic corrosion inhibitors and a fluorine-containing compound. For example, U.S. Pat. No. 5,478,443 to Winebarger et al,

uses a combination of an organic corrosion inhibitor (glycol and dimethylsulfoxide) and fluorine-containing compounds such as ammonium fluoride, hydrogen fluoride and perfluoric acid. U.S. Pat. No. 5,320,709 to Bowden et. al. discloses the use of an anhydrous ammonium fluoride salt in  
5 polyhydric alcohol. The problem with these compositions is that organic solvents are only weak corrosion inhibitors, and a high concentration of organic solvent (greater than 50% by weight) is required. Thus, there is a problem with waste removal since the organic-based cleaning solution is environmentally unfriendly.

10 Therefore, there remains a need for a composition that removes photoresist, plasma etch, and CMP residues from substrates. Additionally, there remains a need for such a composition that does not deleteriously affect the substrate. Further, there remains a need for such a composition that is aqueous-based so that the disposal thereof will not harm the environment.

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### SUMMARY OF THE INVENTION

The present invention is, in brief summary, directed to a non-corrosive cleaning composition that is aqueous based and useful for removing photoresist, plasma etch and CMP residues from a substrate. The composition comprises:

- 20 (i) a hydroxylamine or a hydroxylamine salt compound;  
(ii) at least one fluorine-containing compound; and  
(iii) water.

In an alternative embodiment, this invention contemplates a cleaning  
25 composition comprising:

- (i) a compound selected from the group consisting of an amine, a quaternary ammonium hydroxide and ammonium hydroxide;  
(ii) at least one fluorine-containing compound; and  
(iii) water.

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The invention further contemplates a method of removing residues from a substrate comprising the steps of  
contacting a substrate containing residues with at least one of the above mentioned cleaning compositions.

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#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

A non-corrosive cleaning composition that is useful for removing photoresist, plasma etch and CMP residues from a substrate. The composition preferably comprises:

- 10 (i) a hydroxylamine or a hydroxylamine salt compound;  
(ii) at least one fluorine-containing compound; and  
(iii) water.

The composition can contain either hydroxylamine or a salt of the  
15 hydroxylamine produced by reacting the hydroxylamine with an acid, e.g., nitric acid or sulfuric acid.

Preferred hydroxylamine salts that can be used to form the cleaning composition of the present invention include hydroxylammonium nitrate (also referred to as HAN), hydroxylammonium sulfate (also referred to as HAS), hydroxylammonium  
20 phosphate, hydroxylammonium chloride, hydroxylammonium oxalate, hydroxylammonium citrate, and the like. Alkyl-substituted derivatives of hydroxylammonium salts are also useful; e.g., hydroxyl diethylammonium salts and the like.

25 The fluorine-containing compound in the above composition can be selected from acid fluorides, fluorinated salts, polyammonium fluoride salts and mixtures thereof. Preferred acid fluorides include hydrogen fluoride, (HF), and perfluoric acid. Preferred fluoride salts are ammonium fluoride, ammonium bifluoride, ammonium difluoride and tetraalkyl ammonium fluoride salts such as  
30 tetramethyl ammonium fluoride and tetraethyl ammonium fluoride. Preferably, the

fluorine-containing compound will comprise about 0.5 to 10 wt.% based upon the weight of the composition

5 The polyammonium salts may be prepared by reacting a polyamine with HF to form the polyammonium fluoride salt. For example, HF may be reacted with an aqueous solution of ethylene diamine to form an ethylenediammonium difluoride. Alternatively, an excess amount of HF may be reacted with the polyamine to form the polyammonium salt. Preferred polyammonium salts include ethylenediammonium difluoride and diethylenetriammonium trifluoride.

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It is believed that the fluorine-containing compound aids in removal of contaminants by slightly etching the underlying silicon-based substrate so that any contaminants on the surface or embedded in the substrate are removed. Also, it is believed that many of the plasma etch residues, especially those containing fluoride species, are soluble in fluorine solutions and will also be removed.

15

Hydroxylamines and salts thereof act as corrosion inhibitors and aid in the removal of residues. Thus, the combination of a fluorine compound and a hydroxylamine or hydroxylamine salt has been found by the present applicants to be particularly useful as a cleaning composition.

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The pH of the cleaning composition preferably ranges from weakly acidic to slightly basic so as to not attack or corrode the metal used in the microcircuit fabrication. If the cleaning composition is either too caustic or too acidic, the metal layers on the substrate are subject to attack. Therefore, the components in the cleaning composition should be admixed in appropriate concentrations to provide a composition having a pH with a preferred range from about 2 to 9, and more preferably from about 2 to 6.

25

In a preferred embodiment of this invention, the fluorine-containing compound is admixed with a composition comprising water, a hydroxylamine salt and at least one basic compound selected from the group consisting of: amines,

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quaternary ammonium hydroxides and ammonium hydroxide. Such compositions are described in copending U.S. Patent Application Serial No. 08/709,053, filed September 6, 1996, the subject matter of which is incorporated herein by reference.

5           Amines that may be used as a component in the cleaning compositions include alkanolamines such as monoethanolamine, diethanolamine, triethanolamine, diethylene-glycolamine, N-hydroxyethylpiperazine, and the like. Quaternary ammonium hydroxides that can be used in the compositions include tetraalkylammonium hydroxides having methyl, ethyl, propyl, butyl, hydroxyethyl, 10 and the combinations thereof (e.g., tetramethylammonium hydroxide (hereinafter referred to as TMAH), tetraethyl-ammonium hydroxide, trimethyl hydroxyethylammonium hydroxide, methyl tri (hydroxyethyl) ammonium hydroxide, tetra (hydroxyethyl) ammonium hydroxide, benzyl trimethylammonium hydroxide and the like). Additionally, a combination of ammonium hydroxide 15 with one or more quaternary ammonium hydroxides may also be used. Preferably, the hydroxylamine salt will comprise about 1% to 70% by weight, the base compound will comprise about 0.1% to 10% by weight, and water will comprise the remainder of the composition, these weight percentages being based on the total combined weight of hydroxylamine salt, basic compound and water 20 (excluding the weight of the fluorine-containing compounds and other optional components of the cleaning composition).

          A chelating stabilizer may be optionally included in the cleaning composition to stabilize the hydroxylamine salts. Suitable chelating stabilizers 25 include triethylenetetramine (hereinafter referred to as TETA); 2,2'-[[methyl-1H-benzotriazol-1-yl)methyl]imino]bisethanol (Tradename is IRGAMET 42), (2-benzothiazolythio)succinic acid (Tradename is IRGACOR 252), tricine, bicine, and other water-soluble chelating compounds. Preferably, the stabilizer is present in the composition of the invention in the range of about 5 ppm to about 5000 ppm by 30 weight based on the a total weight of cleaning composition.

A surfactant may also be optionally included in the cleaning composition so as to enhance the power of the plasma etching residue removal from the substrate. Suitable surfactants are selected from nonionic types, cationic types and anionic types of surfactants. Preferably, a surfactant is present in the composition of the invention in the range of about 0.1 ppm to 100 ppm by weight to a total weight of the cleaning composition. The cleaning composition may also, optionally, contain a minor amount of a corrosion inhibitor such as sugar alcohols, catechol and the like.

Another optional agent that may be included in the cleaning composition is a corrosion inhibitor. The preferred corrosion inhibitors are lactic acid, salicyl alcohol, salicyl aldoxime, gallic acid, gallic acid esters and alizarin.

This invention also contemplates a cleaning composition comprising:

- (i) at least one compound selected from the group consisting of: an amine, a quaternary ammonium hydroxide, and ammonium hydroxide;
- (ii) at least one fluorine-containing compound; and
- (iii) water.

The quaternary ammonium hydroxide and fluorine-containing compounds are the same as those described previously in this invention. It is believed that the quaternary ammonium hydroxides are used to remove photoresist residues; while the fluorine-containing compound solubilizes fluorine-containing plasma etch residues and slightly etches the substrate to remove particles on the surface and embedded in the substrate. Other components may also be added in the cleaning composition such as chelating agents, surfactants and corrosion inhibitors as were previously described above.

The pH of the above cleaning composition may range anywhere from weakly acidic to slightly basic so as to not attack or corrode the metal used in the microcircuit fabrication. Therefore, the components in the cleaning composition

should be admixed in appropriate concentrations to maintain the pH range from about 2 to 9.

This invention further contemplates the method of removing residues from  
5 a substrate comprising the steps of:

applying one of the above mentioned cleaning solutions to the substrate containing residues.

The cleaning method of the present invention can also be used in  
10 combination with a dry stripping process if photoresist or other polymer residues remain on the surface. Dry stripping is typically conducted prior to the present cleaning method. Any suitable dry stripping process can be used including O<sub>2</sub> plasma ashing, ozone gas phase-treatment, fluorine plasma treatment, hot H<sub>2</sub> gas treatment (described in U.S. Pat. No. 5,691,117), and the like. The preferred dry  
15 stripping process is O<sub>2</sub> plasma ashing.

Furthermore, the cleaning method can also be used in combination with ozonated water which is used to strip off photoresist and other residues. The ozonated water can be a simple mixture of ozone and ultra-pure water, e.g., DI  
20 water. The ozone can be generated by any conventional means, e.g., an ozone generator. The mixing of the ozone and water may be achieved by any suitable method, such as jetting the ozone into the water by a gas feed nozzle; feeding the water and ozone into a spiral mixer; aspirating the gas into the flow of water; and feeding the ozone into a treatment tank regulated at a given pressure so that ozone  
25 is dissolved into the water. The ozonated water can then be contacted with the substrate by any suitable method such as placing the ozonated water into a tank and submerging the substrates into the ozonated water, or by use of a spray rinse.

While the invention has been described above with reference to specific  
30 embodiments thereof, it is apparent that many changes, modifications and variations can be made without departing from the inventive concept disclosed

herein. Accordingly, it is intended to embrace all such changes, modifications and variations that fall within the spirit and broad scope of the appended claims. All patent applications, patents and other publications cited herein are incorporated by reference in their entirety.

What is claimed is:

1. A cleaning composition comprising:
  - (i) a hydroxylamine or a hydroxylamine salt compound;
  - 5 (ii) at least one fluorine-containing compound; and
  - (iii) water.
2. The composition of claim 1 wherein said fluorine-containing compound is at least one compound selected from the group consisting of:
  - 10 a) an acid fluoride;
  - b) a fluorinated salt; and
  - c) a polyammonium fluoride salt.
3. The composition of claim 1 wherein said hydroxylamine salt  
15 compound is at least one compound selected from the group consisting of:  
hydroxylammonium nitrate, hydroxylammonium sulfate, hydroxylammonium  
phosphate, hydroxylammonium oxalate, hydroxylammonium citrate, and  
hydroxylammonium chloride.
- 20 4. The composition of claim 1 wherein said fluorine-containing  
compound is at least one compound selected from the group consisting of:  
hydrogen fluoride, perfluoric acid, ammonium fluoride, tetramethylammonium  
fluoride, ammonium bifluoride, ethylenediammonium difluoride and  
diethylenetriammonium trifluoride.
- 25 5. The composition of claim 1 further comprising at least one  
additional component selected from the group consisting of: an amine, a quaternary  
ammonium hydroxide and ammonium hydroxide.
- 30 6. The composition of claim 5 wherein said quaternary ammonium  
hydroxide compound is selected from the group consisting of:

tetramethylammonium hydroxide, tetraethylammonium hydroxide, trimethyl hydroxyethylammonium hydroxide, methyl tri (hydroxyethyl) ammonium hydroxide, and tetra(hydroxyethyl)ammonium hydroxide.

5           7.     The composition of claim 4 wherein said amine is selected from the group consisting of: monoethanolamine, diethanolamine, triethanolamine, diethylene glycolamine, and N-hydroxyethylpiperazine.

8.     The composition of claim 1 further comprising a corrosion inhibitor.

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9.     The composition of claim 8 wherein said corrosion inhibitor is selected from the group consisting of: lactic acid, salicyl alcohol, salicyl aldoxime, gallic acid, gallic acid esters, and alizarin.

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10.    The composition of claim 1 further comprising a surfactant.

11.    The composition of claim 1 further comprising a chelating agent.

12.    The composition of claim 1 where the pH is within a range between  
20   about 2 to 6.

13.    A cleaning composition comprising:

- 25           (i) a compound selected from the group consisting of: an amine, a quaternary ammonium hydroxide and ammonium hydroxide,  
            (ii) at least one fluorine-containing compound; and  
            (iii) water.

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14.    The composition of claim 13 wherein said fluorine-containing compound is selected from the group consisting of:

- a) an acid fluoride;  
          b) a fluorinated salt; and



c) a polyammonium fluoride salt.

15. The composition of claim 13 wherein said quaternary ammonium hydroxide compound is selected from the group consisting of:
- 5 tetramethylammonium hydroxide, tetraethylammonium hydroxide, trimethyl hydroxyethylammonium hydroxide, methyl tri (hydroxyethyl) ammonium hydroxide, and tetra(hydroxyethyl)ammonium hydroxide.
16. The composition of claim 13 wherein the fluorine-containing  
10 compound is selected from the group consisting of: hydrogen fluoride, perfluoric acid, ammonium fluoride, tetramethylammonium fluoride, ammonium bifluoride, ethylenediammonium difluoride and diethylenetriammonium trifluoride.
17. The composition of claim 13 wherein said amine is selected from  
15 the group consisting of: monoethanolamine, diethanolamine, triethanolamine, diethylene glycolamine, and N-hydroxyethylpiperazine.
18. The composition of claim 13 further comprising of a corrosion  
20 inhibitor.
19. The composition of claim 18 wherein said corrosion inhibitor is selected from the group consisting of: lactic acid, salicyl alcohol, salicyl aldoxime, gallic acid, gallic acid esters, and alizarin.
20. The composition of claim 13 further comprising a surfactant.
21. The composition of claim 13 further comprising a chelating agent.
22. The composition of claim 13 where the pH ranges is within a range  
30 between about 2 to 9.

23. A method for removing residues from a substrate comprising the step of contacting said residue-containing substrate with said cleaning composition of claim 1.

5 24. The method of claim 23, further comprising a step of subjecting said substrate to dry stripping.

25. The method of claim 23 further comprising the step of contacting said substrate with ozonated water.

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26. A method for removing residues from a substrate comprising the step of contacting said residue -containing substrate with said cleaning composition of claim 13.

15 27. The method of claim 24 further comprising a step of subjecting said substrate to dry stripping.

28. The method of claim 24 further comprising the step of contacting said substrate with ozonated water.

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**AMENDED CLAIMS**

[received by the International Bureau on 1 October 1999 (01.10.99);  
original claims 1- 28 replaced by amended claims 1 -25 (4pages)]

1. A cleaning composition comprising:
  - (i) a hydroxylamine salt compound selected from the group  
5 consisting of hydroxylammonium nitrate, hydroxylammonium phosphate,  
hydroxylammonium oxalate, hydroxylammonium citrate, and  
hydroxylammonium chloride;
  - (ii) at least one fluorine-containing compound; and
  - (iii) water.
- 10 2. The composition of claim 1 wherein said fluorine-containing  
compound is at least one compound selected from the group consisting of:
  - a) an acid fluoride;
  - b) a fluorinated salt; and
  - 15 c) a polyammonium fluoride salt.
3. The composition of claim 1 wherein said fluorine-containing  
compound is at least one compound selected from the group consisting of:  
hydrogen fluoride, perfluoric acid, ammonium fluoride, tetramethylammonium  
20 fluoride, ammonium bifluoride, ethylenediammonium difluoride and  
diethylenetriammonium trifluoride.
4. The composition of claim 1 further comprising at least one  
additional component selected from the group consisting of: an amine, a  
25 quaternary ammonium hydroxide and ammonium hydroxide.
5. The composition of claim 4 wherein said quaternary ammonium  
hydroxide compound is selected from the group consisting of:  
tetramethylammonium hydroxide, tetraethylammonium hydroxide, trimethyl  
30 hydroxyethylammonium hydroxide, methyl tri (hydroxyethyl) ammonium  
hydroxide, and tetra(hydroxyethyl) ammonium hydroxide.

6. The composition of claim 4 wherein said amine is selected from the group consisting of: monoethanolamine, diethanolamine, triethanolamine, diethylene glycolamine, and N-hydroxyethylpiperazine.
- 5
7. The composition of claim 1 further comprising a corrosion inhibitor.
8. The composition of claim 7 wherein said corrosion inhibitor is selected from the group consisting of: lactic acid, salicyl alcohol, salicyl
- 10 aldoxime, gallic acid, gallic acid esters, and alizarin.
9. The composition of claim 1 further comprising a surfactant.
10. The composition of claim 1 further comprising a chelating agent.
- 15
11. The composition of claim 1 where the pH is within a range between about 2 to 6.
12. A cleaning composition comprising:
- 20 (i) A compound selected from the group consisting of: trimethyl hydroxyethylammonium hydroxide, methyl tri (hydroxyethyl) ammonium hydroxide, tetra(hydroxyethyl)ammonium hydroxide, diethylene glycolamine, and N-hydroxyethylpiperazine;
- (ii) at least one fluorine-containing compound; and
- 25 (iii) water.
13. The composition of claim 12 wherein said fluorine-containing compound is selected from the group consisting of:
- a) an acid fluoride;
- 30 b) a fluorinated salt; and
- c) a polyammonium fluoride salt.

14. The composition of claim 12 wherein the fluorine-containing compound is selected from the group consisting of; hydrogen fluoride, perfluoric acid, ammonium fluoride, tetramethylammonium fluoride, ammonium bifluoride, ethylenediammonium difluoride and diethylenetriammonium trifluoride.

15. The composition of claim 12 further comprising of a corrosion inhibitor.

16. The composition of claim 15 wherein said corrosion inhibitor is selected from the group consisting of; lactic acid, salicyl alcohol, salicyl aldoxime, gallic acid, gallic acid esters, and alizarin.

17. The composition of claim 12 further comprising a surfactant.

18. The composition of claim 12 further comprising a chelating agent.

19. The composition of claim 12 where the pH ranges is within a range between about 2 to 9.

20. A method for removing residues from a substrate comprising the step of contacting said residue-containing substrate with said cleaning composition of claim 1.

21. The method of claim 20, further comprising a step of subjecting said substrate to dry stripping.

22. The method of claim 20 further comprising the step of contacting said substrate with ozonated water.

23. A method for removing residues from a substrate comprising the

step of contacting said residue -containing substrate with said cleaning composition of claim 12.

24. The method of claim 23 further comprising a step of subjecting  
5 said substrate to dry stripping.

25. The method of claim 23 further comprising the step of contacting  
said substrate with ozonated water.

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/10881

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :C11D 1/62, 3/24, 3/30

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/175, 176, 178, 201, 202, 203, 204, 210, 212, 245, 254, 255, 256, 257, 259, 412, 477, 480, 504

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, CAPLUS, EUROPATFULL, search terms: hydroxylamine, fluorin?, fluoride, TMAH

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	US 5,855,811 A (GRIEGER et al) 05 January 1999, col. 12, table 1.	13-16 and 22
X	US 4,394,419 A (KONICEK) 19 July 1983, col. 3, lines 29-34.	13, 14, 16, and 22
X	US 5,509,970 A (SHIRAMIZU) 23 April 1996, col. 7, claim 1.	13, 14, and 16
X	US 5,541,037 A (HATAKEYAMA et al) 30 July 1996, col. 6, example 1	13-15
X	US 5,509,970 A (SHIRAMIZU) 23 April 1996, col. 7, claim 1.	13, 14, and 16
X	US 4,215,005 A (VANDER MEY) 29 July 1980, col. 10, example 4.	13, 14, 17, 18, and 20

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"B" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Z" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

24 JUNE 1999

Date of mailing of the international search report

03 AUG 1999

Name and mailing address of the ISA/US  
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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/10881

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3,888,783 A (RODZEWICH) 10 June 1975, col. 6, lines 50-63.	1-4, 8, and 10-12
X	US 5,709,756 A (WARD et al) 20 January 1998, col. 4, example 3.	1, 2, 4, and 8
X, P	US 5,792,274 A (TANABE et al) 11 August 1998, col. 7, examples 5 and 6.	1-9, 11-19, 21 and 22



# INTERNATIONAL SEARCH REPORT

International application N .  
PCT/US99/10881

## Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-22

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/10881

## A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

510/175, 176, 178, 201, 202, 203, 204, 210, 212, 245, 254, 255, 256, 257, 259, 412, 477, 480, 504

## BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-22, drawn to a cleaning composition.

Group II, claim(s) 23-28, drawn to a method for removing residues from a substrate.

The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: Claims 1-22 are either obvious over or anticipated by the prior art. Accordingly, the special technical feature linking the two inventions, a cleaning composition, does not provide a contribution over the prior art, and no single general inventive concept exists. Therefore, restriction is appropriate.